

DESCRIPTION

FLUORINE-CONTAINING VINYL ETHERS, THEIR POLYMERS, AND
RESIST COMPOSITIONS USING SUCH POLYMERS5 BACKGROUND OF THE INVENTION

The present invention relates to fluorine-containing vinyl ethers, their polymers and copolymers, and resist compositions using such polymers and copolymers.

10 Hitherto, fluorine-containing polymers have been used in various fields, since they are superior in heat resistance and chemical resistance. In particular, amorphous fluorine-containing polymers are further superior in transparency, and therefore they have been used and studied in the fields of optical fiber and resist composition (see Japanese Patent Application Publication 2002-201231). In fact, the introduction of fluorine atoms lowers
15 refractive index or improves transparency of the vacuum ultraviolet region light.

In the development of resist compositions (see Y. Kamon et al., J. Photopolym. Sci. Technol., 15, 535 (2002)), now, a major resist type is a positive-type resist composition, in which an acid is generated by light
20 irradiation and then solubility of a resin of the resist composition in alkali aqueous solution changes due to a chemical change of the resin by an action of the acid as a catalyst. In the trend toward shorter wavelength light source to manufacture smaller semiconductor devices, there are problems that resins (e.g., novolak resins and acrylic resins) used in current resists are insufficient
25 in transparency. Thus, there are a demand for polymers that contain fluorine atoms, do not contain structures such as carbonyl, and are superior in heat resistance and solubility in various solvents, and a demand for monomers for synthesizing such polymers.

Recent research and development have revealed that acrylic resins
30 have a possibility to have relatively good resist characteristics (see Y. Kamon

et al., J. Photopolym. Sci. Technol., 15, 535 (2002)). Acrylic resins, however, contain carbonyl structures that absorb vacuum ultraviolet light. Therefore, they are still not sufficient in transparency and are required to achieve further improvement.

5 Since conventional fluorine-containing monomers are inferior in copolymerizability with acrylic or methacrylic esters, it has been difficult to copolymerize acrylic monomers with fluorine-containing monomers. Thus, there are a demand for fluorine-containing monomers that do not have carbonyl structures and are superior in copolymerizability with acrylic or
10 methacrylic monomers and a demand for copolymers of such fluorine-containing monomers and acrylic or methacrylic monomers.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide (a) monomers that can be a raw material for producing polymers, which are low
15 in light scattering and absorption and high in transparency, (b) such polymers, and (c) resist compositions using such polymers.

It is another object of the present invention to provide (a) fluorine-containing copolymers that are low in light scattering and absorption and high in transparency and (b) resist compositions using such copolymers.

20 According to a first aspect of the present invention, there is provided a fluorine-containing vinyl ether represented by the formula 1,



wherein R represents an organic group comprising at least one fluorine atom and a cyclic structure.

25 The organic group (R) of the formula 1 may comprise:

(a) the cyclic structure that is selected from the group consisting of cyclopentane ring, cyclohexane ring, norbornene ring, aromatic rings, tricyclodecane ring; and

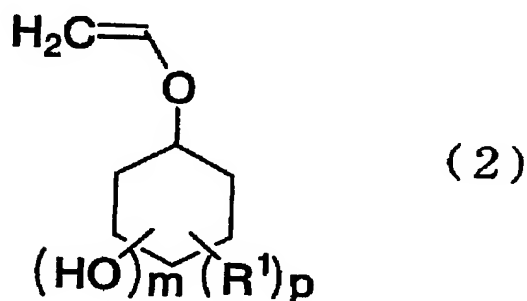
(b) at least one substituent that is selected from the group consisting of $(-\text{OH})_m$, $(-\text{R}^1)_n$, and $-\text{COOR}^4$

where R^1 is at least one substituent selected from the group consisting of $-\text{F}$, $-\text{CF}_3$, and $-\text{R}^2\text{C}(\text{CF}_3)_2\text{OR}^3$, where R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile protecting group,

R^4 is H, a $\text{C}_1\text{-C}_{15}$ alkyl group, or a $\text{C}_1\text{-C}_{15}$ substituent containing an ether bond, and

m is 0 or 1, and n is an integer of 1-8.

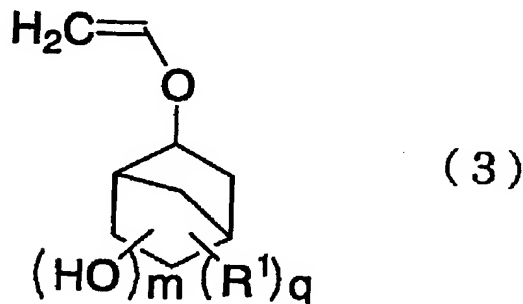
The fluorine-containing vinyl ether of the formula 1 may be represented by the formula 2,



where R^1 is at least one substituent selected from the group consisting of $-\text{F}$, $-\text{CF}_3$, and $-\text{R}^2\text{C}(\text{CF}_3)_2\text{OR}^3$, where R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile protecting group, and

p is an integer of 1-5, and m is 0 or 1.

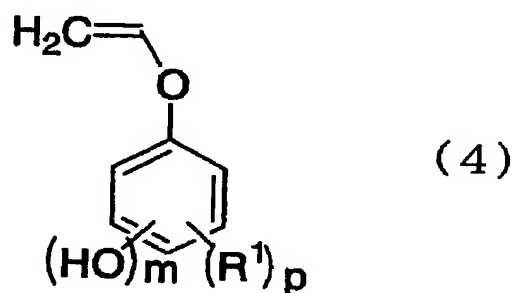
The fluorine-containing vinyl ether of the formula 1 may be represented by the formula 3,



where R^1 is at least one substituent selected from the group consisting of $-F$, $-CF_3$, and $-R^2C(CF_3)_2OR^3$, where R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile protecting group, and

q is an integer of 1-4, and m is 0 or 1.

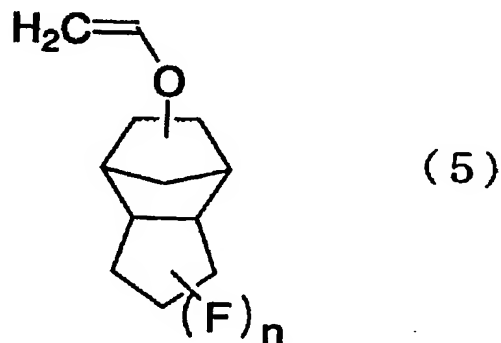
5 The fluorine-containing vinyl ether of the formula 1 may be represented by the formula 4,



where R^1 is at least one substituent selected from the group consisting of $-F$, $-CF_3$, and $-R^2C(CF_3)_2OR^3$, where R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile protecting group, and

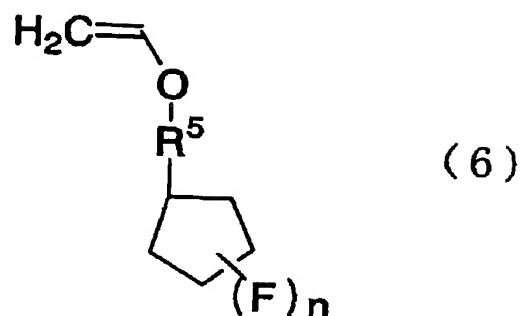
10 p is an integer of 1-5, and m is 0 or 1.

The fluorine-containing vinyl ether of the formula 1 may be represented by the formula 5,



15 where n is an integer of 1-8.

The fluorine-containing vinyl ether of the formula 1 may be represented by the formula 6,



where R^5 is a C_0 - C_5 alkyl group, and n is an integer of 1-8.

The fluorine-containing vinyl ether of the formula 1 may comprise a hexafluoroisopropanol unit represented by the formula 7,



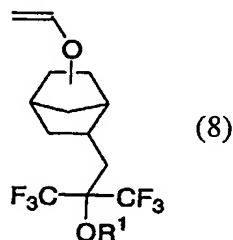
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According to the first aspect of the present invention, there are provided (a) a fluorine-containing polymer comprising a unit derived from the fluorine-containing vinyl ether of the formula 1, and (b) a resist composition comprising this fluorine-containing polymer.

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According to a second aspect of the present invention, there is provided a fluorine-containing copolymer comprising:

a first unit derived from a first monomer that is a fluorine-containing vinyl ether represented by the formula 8:



15 where R^1 is $-H$ or a C_1 - C_8 alkyl group that optionally contains an oxygen atom; and

a second unit derived from a second monomer that is at least one selected from the group consisting of acrylic esters and methacrylic esters.

The second monomer may be a first methacrylic ester represented by the following formula 9.

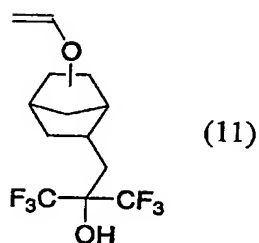
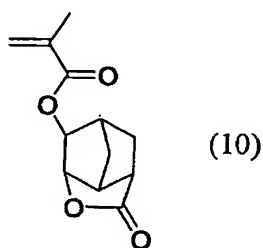
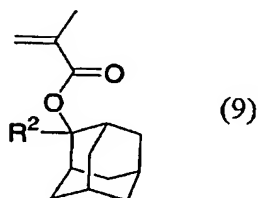
- 5 The second monomer may be an acrylic or methacrylic ester comprising a lactone ring.

The second monomer may be a second methacrylic ester represented by the following formula 10.

- 10 A fluorine-containing copolymer according to the second aspect of the present invention may comprise:

a first unit derived from a first monomer that is a fluorine-containing vinyl ether represented by the formula 11; and

a second unit derived from a second monomer that is a combination of first and second methacrylic esters represented by the formulas 9 and 10,



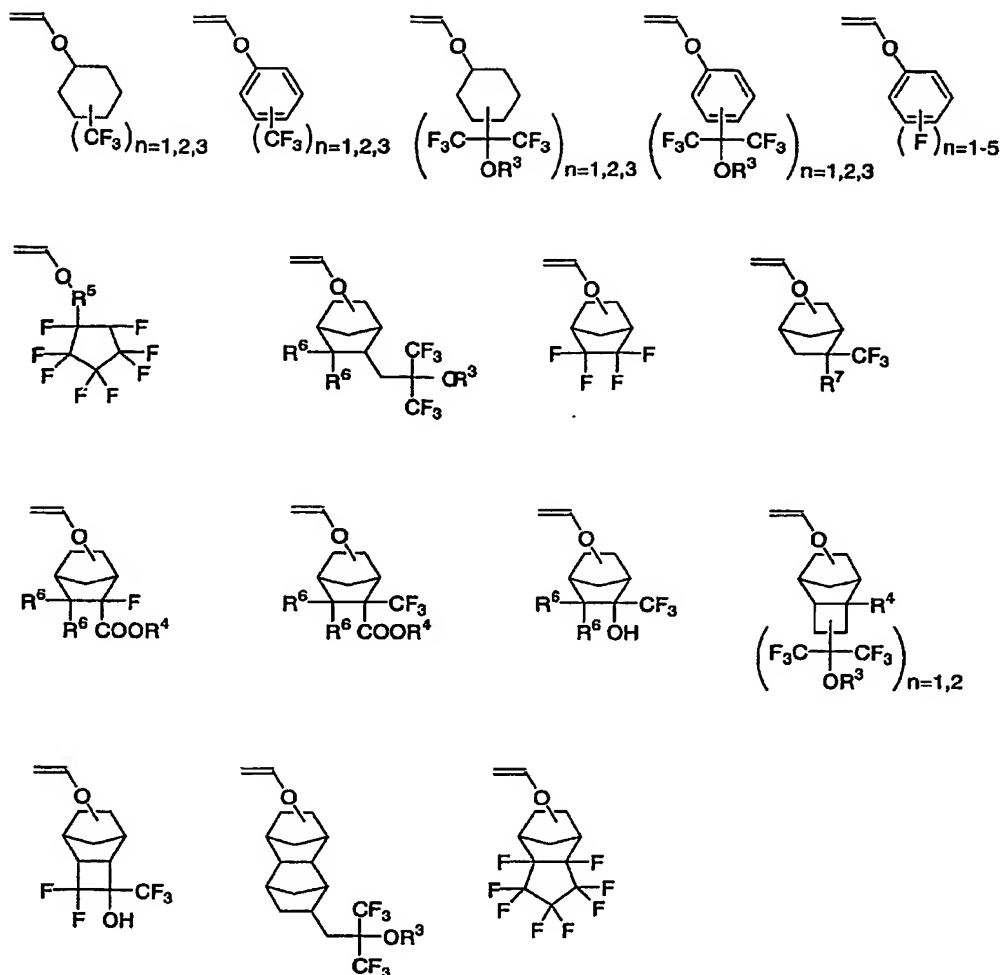
where R^2 is $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_3$.

According to the present invention, there is provided a resist composition comprising a fluorine-containing copolymer of the second aspect of the present invention.

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The first aspect of the present invention is described in detail, as follows. The inventors unexpectedly found that a novel fluorine-containing vinyl ether according to the first aspect of the present invention is free from the above-mentioned conventional problems. Specifically, it was found that
10 the fluorine-containing vinyl ether is capable of producing homopolymers and copolymerizing with various monomers, and that the resulting fluorine-containing polymers dissolve in various organic solvents and have high transparency. Therefore, they are useful as transparent resist compositions.

15 Specific examples of the fluorine-containing vinyl ether include those represented by the following structural formulas:



where R^3 is H or an acid-labile protecting group;

R^4 is H, a C_1 - C_{15} alkyl group, or a C_1 - C_{15} substituent having an ether bond;

5 R^5 is a C_0 - C_5 alkyl group;

R^6 is H or F; and

R^7 is CF_3 , OH, CO_2H , CO_2R^8 , or $OCOR^8$ where R^8 is C_1 - C_{15} alkyl group.

Of the fluorine-containing vinyl ethers represented by the above
 10 structural formulas, those containing a hexafluoroisopropanol unit
 ($-C(CF_3)_2-OH$) or hexafluoroisopropanol derivative unit ($-C(CF_3)_2-OR^3$, where

R³ is a hydrogen or acid-labile protecting group optionally containing a hetero atom(s) such as oxygen) serve to improve adhesion of the resulting polymer to substrate. Examples of such acid-labile protecting group include t-butoxycarbonyl group, methoxymethyl group, 2-methyl-2-adamantyl ester group, and 2-ethyl-2-adamantyl ester group. Of fluorine-containing vinyl ethers, those containing structures, such as bicyclo[2.2.1]heptane and tricyclodecane, are preferable since polymers derived from those vinyl ethers are low in light absorption caused by double bond and are superior in heat resistance.

It is possible to apply various known processes to produce the fluorine-containing vinyl ether of the present invention. For example, it is possible to treat a fluorine-containing alcohol with an alkali metal, followed by a reaction with acetylene or vinyl halide. As this alkali metal, it is possible to use various alkali metal compounds, such as sodium hydride, potassium hydride, sodium hydroxide, potassium hydroxide, and potassium carbonate.

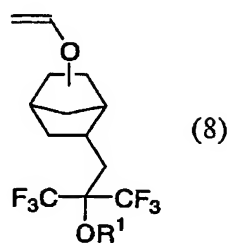
It is known to synthesize vinyl ethers by vinyl exchange reaction using palladium as catalyst. This vinyl exchange reaction is conducted in the presence of a vinyl ether or alcohol to obtain the target vinyl ether. In particular, it is preferable to use a palladium catalyst, since reaction conditions become mild and since side reactions do not easily occur. It is possible to use a bivalent palladium such as palladium acetate Pd(OAc)₂ as the palladium catalyst. It is also possible to use a ligand (to be bonded to palladium) for the purpose of controlling the reaction activity of palladium. The type of this ligand is not particularly limited. Preferable examples of this ligand include nitrogen-containing bidentate ones (e.g., 2,2'-bipyridyl and 1,10-phenanthroline) since the amount of by-products is small. It is possible to react palladium with ligand prior to the vinyl exchange reaction. Alternatively, it is possible to separately add palladium and ligand to the reaction system upon the vinyl exchange reaction to make ligand bonded to palladium.

It is possible to use a reaction solvent in the process for producing the fluorine-containing vinyl ether. This solvent is not particularly limited, as long as it does not interfere with the target reaction. Its examples include common organic solvents such as tetrahydrofuran, diethyl ether, and
5 dimethylformamide. Furthermore, the solvent can be a vinyl ether that is the substrate of the vinyl exchange reaction. In this case, a fluorine-free vinyl ether is used as the reaction substrate and as the reaction solvent in the reaction with a fluorine-containing alcohol, thereby obtaining a fluorine-containing vinyl ether. Although the reaction temperature is not
10 particularly limited, it is preferably in a range of -80°C to $+200^{\circ}\text{C}$, more preferably in a range of -30°C to $+150^{\circ}\text{C}$, in view of reaction and handling easiness of peripheral devices. The reaction product can be separated and purified by a common process, such as concentration, extraction, distillation, recrystallization, filtration, column chromatography, and combinations of
15 these.

The second aspect of the present invention is also explained in detail in the following. The inventors unexpectedly found that a novel fluorine-containing copolymer according to the second aspect of the present invention is free from the above-mentioned conventional problems.
20 Specifically, it was found that a fluorine-containing vinyl ether (represented by the formula 8) is capable of copolymerizing with various acrylic and methacrylic monomers and that the resulting fluorine-containing copolymer dissolves in various organic solvents and has high transparency.

As stated above, the fluorine-containing copolymer according to the
25 second aspect of the present invention comprises:

a first unit derived from a first monomer that is a fluorine-containing vinyl ether represented by the formula 8:



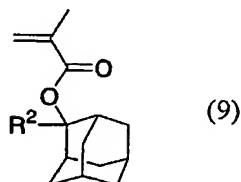
where R¹ is -H or a C₁-C₈ alkyl group that optionally contains an oxygen atom; and

a second unit derived from a second monomer that is at least one
5 selected from the group consisting of acrylic esters and methacrylic esters.

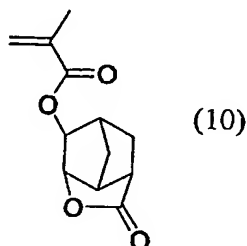
When the first monomer contains a hexafluoroisopropanol unit (-C(CF₃)₂-OH), the resulting copolymer is improved in transparency due to fluorine atoms, in adhesion to substrate, and in solubility in alkali aqueous solution upon development of resist composition.

10 The acrylic or methacrylic ester as the second monomer is not limited in structure. For example, it may contain halogen (e.g., fluorine), an alkyl group optionally containing fluorine, or a ring structure (e.g., adamantane ring, norbornene ring, and lactone ring) optionally containing a functional group (e.g., alcohol and carboxylic acid). The acrylic or methacrylic ester
15 may be one having at its side chain an alkyl group optionally containing fluorine or one having a hexafluorocarbonol group.

In order to achieve characteristics as positive-type resist, the acrylic or methacrylic ester may be one containing an acid-labile protecting group, such as t-butyl acrylate, t-butyl methacrylate, 2-methyladamantyl acrylate, and
20 2-ethyladamantyl acrylate. For example, an adamantane-structure-containing methacrylic ester represented by the formula (9) is preferable to improve etching resistance,

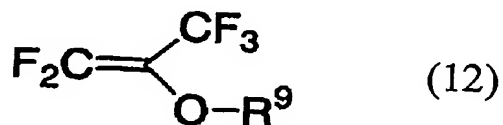


where R^2 is $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_3$. As another example, a methacrylic ester represented by the formula (10) is preferable to improve etching resistance and adhesion of the fluorine-containing copolymer to substrate.



- 5 The following descriptions are common to a fluorine-containing polymer according to the first aspect of the present invention and a fluorine-containing copolymer according to the second aspect of the present invention, unless otherwise specified. The polymer according to the first aspect of the present invention is defined as a polymer (homopolymer or
- 10 copolymer) containing a unit derived from the fluorine-containing vinyl ether.
- In the first and second aspects of the present invention, comonomer used for preparing the fluorine-containing copolymer is not particularly limited. In fact, comonomer according to the first aspect of the present invention is defined as monomer other than the fluorine-containing vinyl
- 15 ether (represented by the formula 1). In contrast, comonomer according to the second aspect of the present invention is defined as monomer other than the first and second monomers. It is possible to use a combination of several comonomers. Examples of such comonomer include α -olefins (e.g., ethylene and propylene), cyclic olefins (e.g., norbornene and cyclohexene), vinyl ethers
- 20 other than the fluorine-containing vinyl ether of the invention, vinyl esters, acrylic or methacrylic acid, acrylic or methacrylic ester, α -trifluoromethylacrylic acid, α -trifluoromethylacrylic ester, allyl ether, styrene, vinyl silane, anhydrous maleic acid, and acrylonitrile. The comonomer may contain at least one selected from fluorine atoms,
- 25 heteroatoms (e.g., oxygen), functional groups, cyclic structure organic groups (e.g., adamantyl group), and reactive groups that are released by the action of

acid. Furthermore, it is possible to use fluoroolefins such as tetrafluoroethylene, chlorotrifluoroethylene, hexafluoroisobutene, hexafluoropropylene, trifluoroethylene, perfluorovinyl ether, octafluorocyclopentene, and an olefin represented by the following formula 12.



wherein R^9 represents an alkyl group having a carbon atom number of from 1 to 15 and may contain a heteroatom(s) such as oxygen.

10 In the first aspect of the present invention, the ratio of the fluorine-containing vinyl ether to the comonomer in the preparation of the fluorine-containing copolymer is not particularly limited. The fluorine-containing copolymer contains the unit derived from the fluorine-containing vinyl ether in an amount of preferably 0.1mol% or greater, more preferably 1mol% or greater, in order to improve the fluorine-containing copolymer in transparency.

15 In the second aspect of the present invention, the ratio of the first monomer (fluorine-containing vinyl ether represented by the formula 8) to the second monomer in the preparation of the fluorine-containing copolymer is not particularly limited. The fluorine-containing copolymer contains each of the first and second units in an amount of preferably 0.1mol% or greater, more preferably 1mol% or greater, in order to show high transparency and high resolution. Thus, comonomer is more preferably in an amount of 98mol% or less.

25 The number average molecular weight of the fluorine-containing polymer or copolymer may be from 1,000 to 1,000,000, preferably from 2,000 to 100,000. If it is too small, the fluorine-containing polymer or copolymer may become insufficient in strength and inferior in heat resistance in the use for various compositions. If it is greater than 100,000, it may become inferior in solubility in solvent.

The process for producing the fluorine-containing polymer or copolymer is not particularly limited. It can be a known polymerization such as anionic polymerization, radical polymerization, ion polymerization or coordination polymerization. Of these, radical polymerization is preferably
5 used. The polymerization can be conducted by a known manner such as bulk polymerization, solution polymerization, suspension polymerization or emulsion polymerization.

The temperature for conducting the polymerization can be suitably set depending on the polymerization process, polymerization manner and the
10 type of the polymerization initiator. It may be 20-200°C, preferably 40-120°C.

The radical polymerization initiator for conducting the radical polymerization is not particularly limited. Its examples include azo compounds, peroxides and redox compounds.

It is optional to use a polymerization solvent in the polymerization for
15 producing the fluorine-containing polymer or copolymer. Although the polymerization solvent is not particularly limited, it is preferably one that does not greatly interfere with the polymerization. Its typical examples are ketones such as acetone; aromatic solvents such as toluene; cyclic hydrocarbon solvents such as cyclohexane; alcohols such as isopropyl alcohol; esters such
20 as butyl acetate; and ethers such as tetrahydrofuran. Furthermore, it is possible to use a molecular weight adjusting agent, such as mercaptan, in the polymerization.

The polymerization may be conducted by radical emulsion polymerization, as stated above, using an emulsifying agent. This
25 emulsifying agent may be an anion and/or nonion emulsifying agent. The radical polymerization initiator usable in the emulsion polymerization is not limited to a particular type. A water-soluble initiator such as persulfate is preferably used.

The suspension stabilizer for conducting suspension polymerization is
30 not particularly limited. It is possible to use a water-soluble polymer such as methylcellulose.

The fluorine-containing vinyl ether of the present invention is useful as a raw material monomer for transparent polymers for coating use. The resulting fluorine-containing polymers and copolymers can be applied to various fields as transparent polymers. They are useful as resist compositions for producing semiconductors and as anti-reflection film materials. Furthermore, they are useful as core materials, cladding materials, covering materials, and optical bonds for resin optical fibers and optical waveguides.

The use of the fluorine-containing polymer or copolymer is not particularly limited in the resist uses. For example, it can be used as a polymer that changes solubility in alkali aqueous solution by the generation of acid or amine. Such polymer can be applied to both of positive-type and negative-type resist compositions. Such polymer can be prepared by introducing an acid-labile protecting group into at least one of the fluorine-containing vinyl ether and the comonomer(s).

For example, it is possible to prepare a resist by using an organic solvent, a photoacid generator, and an additive(s), in addition to the fluorine-containing polymer. Furthermore, it is optional to add another polymer to prepare a resin blend resist.

The fluorine-containing polymer or copolymer according to the present invention may be formed into a film by dissolving the polymer or copolymer in a solvent to prepare a coating solution and then by applying the coating solution to a substrate. This solvent is not particularly limited as long as the polymer or copolymer can be dissolved therein. Its examples include ketones such as acetone and methyl ethyl ketone; polyhydric alcohols and their derivatives such as ethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, and propylene glycol monomethyl ether acetate; ethers such as tetrahydrofuran and dioxane; esters such as ethyl acetate, butyl acetate, methyl lactate, and ethyl lactate; aromatic solvents such as xylene and toluene; and fluorine-containing solvents such as fleon. The solvent for

preparing the coating solution may be a single solvent or a mixture of at least two solvents.

The above-mentioned photoacid generator for a resist composition is not particularly limited. It can be suitably selected from acid generators for chemically amplified resists. Examples of such acid generators include 5
bissulfonyldiazomethanes, nitrobenzyl derivatives, onium salts, halogen-containing triazine compounds, cyano group-containing oximesulfonate compounds, and other oximsulfonate compounds. The acid generator may be used in the form of a single compound or a mixture of at least two compounds. The content of the acid generator in the resist 10
composition may be 0.5-20 parts by weight, relative to 100 parts by weight of the polymer or copolymer.

According to need, it is optional to add an additive to the polymer or copolymer. Examples of such additive include solubility inhibitor, plasticizer, 15
stabilizer, coloring agent, light amplifier, surfactant, tackifier, leveling agent, deforming agent, adhesion enhancing agent, and quencher.

The above-mentioned resist composition according to the present invention can be used in conventional resist patterning methods, as exemplified in the following. Firstly, a solution of the resist composition is 20
applied to a supporting member (e.g., silicon wafer) by spin coating, followed by drying to form a photosensitive layer. Then, the photosensitive layer is exposed to a light from an exposure apparatus through a mask pattern, followed by heating. Then, a development treatment is conducted by using an alkali aqueous solution, thereby obtaining a resist pattern conforming to 25
the mask pattern.

It is possible to apply a solution of the fluorine-containing polymer or copolymer to substrate, followed by drying and according to need heating, in order to form an anti-reflection film having a thickness for showing anti-reflection.

The following nonlimitative examples are illustrative of the present invention. The following Examples 1-1 to 1-10 are illustrative of the first aspect of the present invention.

EXAMPLE 1-1

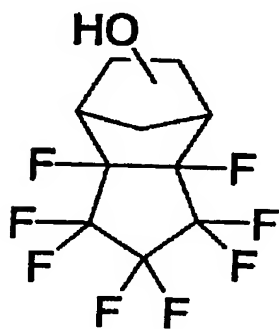
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SYNTHESIS OF PALLADIUM CATALYST

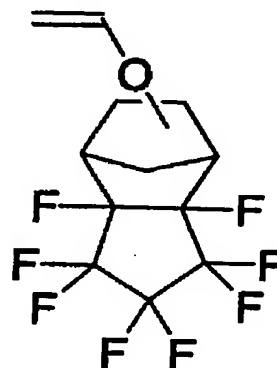
A 100mL glass container was charged with 11.2g of palladium acetate and 1L of toluene. Then, a solution prepared by dissolving 8g of dipyrldyl in 200mL of toluene was gradually added, followed by stirring for 10min. The resulting precipitate was filtered, washed with ether, and recrystallized from 10 500mL of dichloromethane. 3hr later, the crystals were taken out by filtration, followed by vacuum drying for 12hr, thereby preparing a palladium catalyst.

SYNTHESIS OF VINYL ETHER 1

A 100mL glass container was charged with 2.96g of an alcohol 1 15 represented by the following formula, 0.19g of the palladium catalyst obtained by Synthesis of Palladium Catalyst, and 19mL of ethyl vinyl ether, followed by stirring under cooling in water bath for 24hr. The reaction mixture was filtered through Cellite, followed by washing with water and saturated brine, drying with anhydrous magnesium sulfate, and distilling the solvent off, 20 thereby obtaining 1.7g of the target compound, a vinyl ether 1 represented by the following formula, through silica gel chromatography.



Alcohol 1



Vinyl ether 1

The vinyl ether 1 was a mixture of two kinds of stereoisomers. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy. The obtained data are as follows.

^1H NMR (CDCl_3 , standard: TMS, 400MHz)

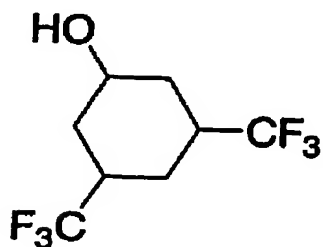
5 δ 1.70-1.73 (m, 2H), 2.0-2.5 (m, 2H), 2.8-3.8 (m, 2H), 4.1-4.5 (m, 3H), and 6.29 (dd, $J=6.8, 14.4\text{Hz}$, 0.4H) for Stereoisomer 1 and 6.31 (dd, $J=6.8, 14.4\text{Hz}$, 0.6H) for Stereoisomer 2.

MS m/z (%) 322 (M^+ , 100), 239(36), 95(45).

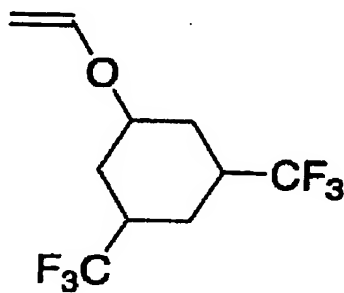
EXAMPLE 1-2

10 SYNTHESIS OF VINYL ETHER 2

Example 1-1 was repeated except in that a 100mL glass container was charged with 2.36g of an alcohol 2 represented by the following formula, 0.19g of the palladium catalyst obtained by Synthesis of Palladium Catalyst, and 26mL of t-butyl vinyl ether, followed by stirring at reflux temperature for 4hr, 15 thereby obtaining 1.2g of the target compound, a vinyl ether 2 represented by the following formula. The obtained data are as follows.



Alcohol 2



Vinyl ether 2

^1H NMR (CDCl_3 , standard: TMS, 400MHz)

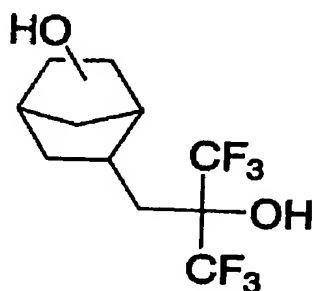
20 δ 1.3-1.4 (m, 3H), 2.1-2.3 (m, 3H), 2.32-2.36 (m, 2H), 3.72-3.83 (m, 1H), 4.11 (dd, $J=2.0, 6.6\text{Hz}$, 1H), 4.34 (dd, $J=2.0, 14.0\text{Hz}$, 1H), 6.30 (dd, $J=6.6, 14.0\text{Hz}$, 1H)

MS m/z (%) 262 (M^+ , 47), 199(75), 109(100).

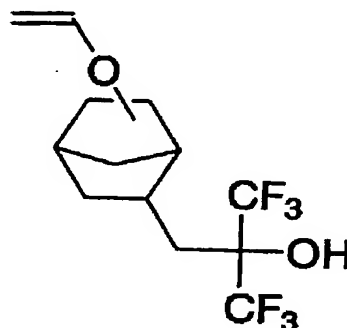
EXAMPLE 1-3

SYNTHESIS OF VINYL ETHER 3

Example 1-1 was repeated except in that 2.96g of the alcohol 1 were replaced with 2.92g of an alcohol 3 represented by the following formula, thereby obtaining 1.2g of the target compound, a vinyl ether 3 represented by the following formula. The obtained data are as follows.



Alcohol 3



Vinyl ether 3

^1H NMR (CDCl_3 , standard: TMS, 400MHz)

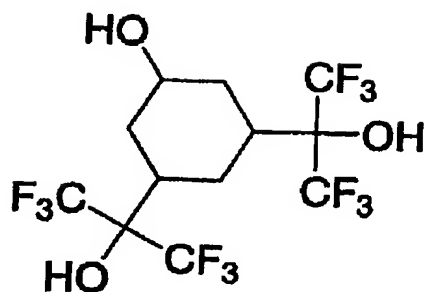
δ 1.1-2.3 (m, 11H), 2.85-2.95 (m, 1H), 3.81-3.88 (m, 1H), 3.98-4.01 (m, 1H), 4.11-4.19 (m, 1H), 6.31 (dd, $J=6.8, 14.4\text{Hz}$, 1H)

MS m/z (%) 318 (M^+ , 41), 275(100), 233(28)

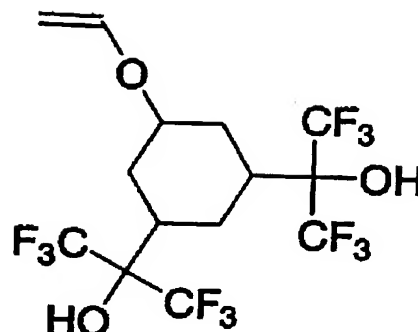
EXAMPLE 1-4

SYNTHESIS OF VINYL ETHER 4

Example 1-1 was repeated except in that a 100mL glass container was charged with 4.32g of an alcohol 4 represented by the following formula, 0.19g of the palladium catalyst obtained by Synthesis of Palladium Catalyst, and 19mL of ethyl vinyl ether, followed by stirring under cooling in water bath for 3hr, thereby obtaining 1.1g of the target compound, a vinyl ether 4 represented by the following formula. The obtained data are as follows.



Alcohol 4



Vinyl ether 4

^1H NMR (CDCl_3 , standard: TMS, 400MHz)

δ 1.1-1.6 (m, 4H), 2.31 (d, $J=14.0\text{Hz}$, 2H), 2.42-2.50 (m, 2H), 3.13 (s, 2H), 4.12 (dd, $J=1.6, 6.8\text{Hz}$, 1H), 4.29-4.32 (m, 1H), 4.35 (dd, $J=1.6, 14.0\text{Hz}$, 1H), 6.27 (dd, $J=6.8, 14.0\text{Hz}$, 1H)

MS m/z (%) 458 (M^+ , 1), 377(19), 247(100).

EXAMPLE 1-5

A 10mL pressure-proof container was charged with 0.64g of the vinyl ether 1 of Example 1-1, 0.007g of di-*t*-butylperoxypivalate, and 0.13g of butyl acetate, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid using 30mL of *n*-hexane, followed by filtration and vacuum drying, thereby obtaining 0.07g of a white polymer. The obtained polymer was found by gel permeation chromatography (GPC) using polystyrene as a standard to have a weight average molecular weight of 5,000. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 98% at 193nm wavelength.

EXAMPLE 1-6

A 10mL pressure-proof container was charged with 0.32g of the vinyl

ether 3 of Example 1-3 and 0.003g of azobisisobutyronitrile, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 0.5g of butyl acetate were added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated using 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.05g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 5,600. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 99% at 193nm wavelength.

EXAMPLE 1-7

A 10mL pressure-proof container was charged with 0.48g of the vinyl ether 1 of Example 1-1, 0.29g of α -trifluoromethylacrylic t-butyl ester (hereinafter TFMA-B), 0.01g of di-t-butylperoxypivalate, and 0.16g of butyl acetate, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 1g of butyl acetate were added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated using 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.52g of a white polymer. The obtained polymer was found by GPC using polystyrene as a standard to have a weight average molecular weight of 48,200. The polymer was found by ^{19}F NMR peak strength to contain 47 mol% of a unit derived from the vinyl ether 1 and 53 mol% of a unit derived from the TFMA-B. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 98% at 193nm wavelength.

EXAMPLE 1-8

A 50mL pressure-proof container was charged with 0.48g of the vinyl

ether 1 of Example 1-1, 0.32g of octafluorocyclopentene (hereinafter "OFCPE"), 0.01g of di-t-butylperoxypivalate, and 0.21g of butyl acetate, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 1g of butyl acetate were added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated using 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.41g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 4,800. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 99% at 193nm wavelength.

EXAMPLE 1-9

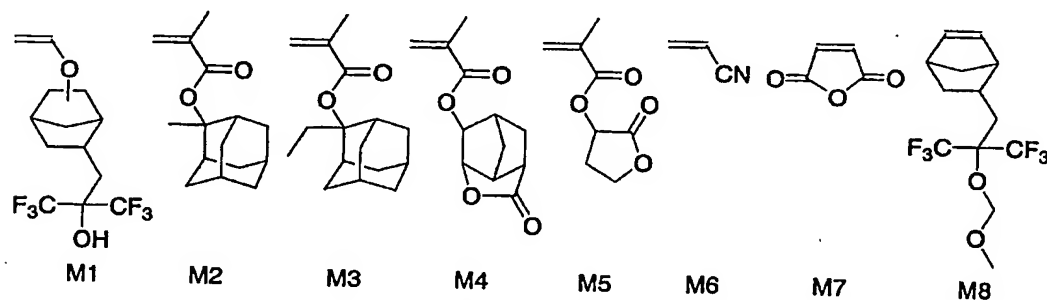
A 10mL pressure-proof container was charged with 0.48g of the vinyl ether 3 of Example 1-3, 0.29g of TFMA-B, 0.01g of di-t-butylperoxypivalate, and 0.16g of butyl acetate, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 1g of butyl acetate were added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated using 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.55g of a white polymer. The obtained polymer was found by GPC using polystyrene as a standard to have a weight average molecular weight of 7,600. The polymer was found by ¹⁹F NMR peak strength to contain 50 mol% of a unit derived from the vinyl ether 3 and 50 mol% of a unit derived from the TFMA-B. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 99% at 193nm wavelength.

EXAMPLE 1-10

The polymer obtained in Example 1-9 was dissolved in propylene glycol monomethyl ether acetate to have a solid matter concentration of

10wt%. Then, an acid generator, triphenylsulfonium triflate made by Midori Kagaku Co., Ltd., was dissolved in an amount of 2 parts by weight per 100 parts by weight of the polymer, followed by filtration with 0.2 μ m membrane filter, thereby preparing a resist solution. This resist solution was applied to a silicon wafer by spin coating to form a resist film having a thickness of 500nm. Then, the resist film was subjected to a preliminary baking at 110°C, followed by exposure at 248nm using a KrF excimer laser and then by a post exposure baking at 120°C. Then, the resist film was developed by a puddle development at 23°C for 1 minute using 2.38 wt% tetramethylammonium hydroxide aqueous solution, followed by washing with pure water and drying. As a result, the non-exposed portion was not dissolved by the tetramethylammonium hydroxide aqueous solution, but the laser exposed portion was completely dissolved thereby. In other words, the resist film was found to have a necessary positive-type resist behavior.

The following Examples 2-1 to 2-7 are illustrative of the second aspect of the present invention. Monomers represented by the following formulas were used in Examples 2-1 to 2-7.



EXAMPLE 2-1

A 50mL glass container was charged with 5.0g of monomer M1, 1.58g of monomer M2, 0.16g of di-*t*-butylperoxypivalate, and 6.6g of butyl acetate, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid using 1L of *n*-hexane, followed by filtration and vacuum drying.

thereby obtaining 3.7g of a white polymer. The obtained polymer was found by gel permeation chromatography (GPC SYSTEM-11 (trade name) made by Shodex) using polystyrene as a standard to have a weight average molecular weight of 25,400. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 98% at 193nm wavelength.

EXAMPLE 2-2

A 50mL glass container was charged with 5.0g of monomer M1, 1.67g of monomer M3, 0.23g of di-t-butylperoxyvalate, and 6.7g of butyl acetate. Then, the same procedures as those of Example 2-1 were conducted, thereby obtaining 3.5g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 20,100. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 97% at 193nm wavelength.

EXAMPLE 2-3

A 50mL glass container was charged with 2.5g of monomer M1, 1.84g of monomer M2, 0.88g of monomer M4, 0.20g of azobisisobutyronitrile, and 26g of toluene, followed by replacing the inside atmosphere of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 65°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid using 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.4g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 15,000. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 95% at 193nm wavelength.

EXAMPLE 2-4

A 50mL glass container was charged with 2.5g of monomer M1, 1.84g

of monomer M2, 0.21g of monomer M6, 0.20g of azobisisobutyronitrile, and 23g of toluene. Then, the same procedures as those of Example 2-3 were conducted, thereby obtaining 3.4g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 19,000. The
5 polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 96% at 193nm wavelength.

EXAMPLE 2-5

A 50mL glass container was charged with 2.5g of monomer M1, 1.84g
10 of monomer M2, 0.77g of monomer M7, 0.20g of azobisisobutyronitrile, and 26g of toluene. Then, the same procedures as those of Example 2-3 were conducted, thereby obtaining 3.1g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 13,000. The
15 polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film was found to have a light transmittance of 96% at 193nm wavelength.

EXAMPLE 2-6

A 50mL glass container was charged with 2.5g of monomer M1, 0.53g
of monomer M5, 1.50g of monomer M8, 0.20g of azobisisobutyronitrile, and
20 23g of toluene. Then, the same procedures as those of Example 2-3 were conducted, thereby obtaining 2.7g of a white polymer. The obtained polymer was found to have a weight average molecular weight of 8,000. The polymer was soluble in propylene glycol monomethylacetate. The resulting solution was applied to a substrate to form a film of 100nm thickness, and this film
25 was found to have a light transmittance of 99% at 193nm wavelength.

EXAMPLE 2-7

Example 1-10 was repeated except in that the polymer obtained in Example 1-9 was replaced with that obtained in Example 2-3 and that the exposure was conducted at 193nm using an ArF excimer laser. As a result,
30 the non-exposed portion was not dissolved by the tetramethylammonium hydroxide aqueous solution, but the laser exposed portion was completely

dissolved thereby. In other words, the resist film was found to have a necessary positive-type resist behavior.

The entire disclosure of each of Japanese Patent Application Nos. 2002-320871 filed on November 5, 2002 and 2003-022925 filed on January 31,
5 2003, including specification, claims, summary and drawings, is incorporated herein by reference in its entirety.